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Unusual Behavior of Two-Photon Absorption from Three-Level Molecules in a One-Dimensional Lattice

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We derive an analytical expression for the two-photon absorption spectrum of a one-dimensional lattice of three-level molecules. This result enables us to investigate the interference between collective and intramolecular effects in the nonlinear optical response of molecular aggregates. We find that, depending on the system parameters, the third molecular level gives rise to zero, one, or two additional peaks in the two-photon absorption spectrum.

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Exactly solvable models have always taken a special place in many-body theory. A well-known example is the chain of N two-level molecules with nearest-neighbor transfer interactions, which is equivalent to the one-dimensional spin-$\frac{1}{2}$ XY model in a magnetic field. For this system, all 2^N eigenstates and energies can be calculated using the Jordan-Wigner transformation [1]. Historically, this model has played an important role in the study of magnetic systems [2]. Recently, it has been utilized in describing the nonlinear optical response of molecular aggregates, making it possible to exactly calculate multiphoton processes involving multiexciton states (eigenstates with two or more excited molecules) [3,4]. Within this description, two-photon absorption (TPA) necessarily involves two molecules and therefore strongly depends on intermolecular interactions. By contrast, in more realistic assemblies of interacting *multilevel* molecules, TPA can also have a large *intramolecular* component, where two photons double excite a single molecule. The distinction between these two sources of nonlinearity, in addition to being of great interest in the design of molecular nonlinear optical devices, is of direct relevance to the interpretation of the induced absorption features found in recent pump-probe experiments on J aggregates [5]. It is also noteworthy that the competition between these two mechanisms has been studied experimentally in clusters of aromatic molecules, where multiphoton ionization rates were shown to depend strongly on the intermolecular mechanism via exciton-exciton annihilation [6,7].

The purpose of this Letter is to study the interference of collective and individual effects in nonlinear spectra by considering a chain of three-level molecules. Although no exact solution exists for all 3^N eigenstates of this system, we will show that it *is* possible to derive a closed analytic form for the TPA spectrum. We analyze the general result as a function of the system parameters and find unusual behavior when the second excited state is nearly resonant with twice the first one.

Consider a linear chain of identical centrosymmetric three-level molecules, with lattice constant a. The molecular ground, first, and second excited states have energies zero, $\hbar\omega_b$, and $\hbar\omega_a$, respectively, and are denoted $|0_n\rangle$, $|b_n\rangle$, and $|a_n\rangle$, where n $(= 1,\ldots,N)$ labels the molecules. The states alternate in inversion symmetry, starting with gerade symmetry in the ground state. Hence a direct transition from $|0_n\rangle$ to $|a_n\rangle$ is not allowed. Excitations from $|0_n\rangle$ to $|b_n\rangle$ and from $|b_n\rangle$ to $|a_n\rangle$ occur through the transition dipoles $\boldsymbol{\mu}_1$ and $\boldsymbol{\mu}_2$, respectively. It is assumed that all dipoles are parallel, making an angle θ with the chain axis. Thus, $\boldsymbol{\mu}_1$ is also parallel to $\boldsymbol{\mu}_2$, an assumption which merely simplifies our resulting expressions, but is not necessary to obtain an analytical solution. The dipole-dipole coupling between neighboring molecules gives rise to (i) energy transfer, $|b_n 0_{n\pm1}\rangle \rightarrow |0_n b_{n\pm1}\rangle$, with strength $J = \mu_1^2(1 - 3\cos^2\theta)/a^3$ and (ii) exciton-exciton annihilation, $|b_n b_{n\pm1}\rangle \rightarrow |a_n 0_{n\pm1}\rangle$ or $|0_n a_{n\pm1}\rangle$, with strength $\tilde{J} = J\mu_2/\mu_1$. The second process attains optimal efficiency when ω_a is in the order of $2\omega_b$, which is assumed throughout. Other nonresonant dipole-dipole interactions, as well as all non-nearest-neighbor contributions, are neglected. We then arrive at the following Hamiltonian for our system:

$$\hat{H} = \hat{H}_b + \hat{H}_a\hat{H}_{ab}\,, \tag{1a}$$

$$\hat{H}_b = \hbar\omega_b \sum_{n=1}^{N} \hat{b}_n^\dagger \hat{b}_n + \hbar J \sum_{n=1}^{N} (\hat{b}_n^\dagger \hat{b}_{n+1} + \hat{b}_{n+1}^\dagger \hat{b}_n)\,, \tag{1b}$$

$$\hat{H}_a = \hbar\omega_a \sum_{n=1}^{N} \hat{a}_n^\dagger \hat{a}_n\,, \tag{1c}$$

$$\hat{H}_{ab} = \hbar\tilde{J} \sum_{n=1}^{N} (\hat{a}_n^\dagger + \hat{a}_{n+1}^\dagger)\hat{b}_n\hat{b}_{n+1} + \text{H.c.}\,, \tag{1d}$$

where periodic boundary conditions are assumed. $\hat{b}_n^\dagger$ $(\hat{b}_n)$ and $\hat{a}_n^\dagger$ $(\hat{a}_n)$ are exciton creation (annihilation) operators with the following properties: $\hat{a}_n^\dagger|0_n\rangle = |a_n\rangle$, $\hat{b}_n^\dagger|0_n\rangle = |b_n\rangle$, and $\hat{a}_n^\dagger\hat{b}_n^\dagger|0_n\rangle = \hat{b}_n^\dagger\hat{a}_n^\dagger|0_n\rangle = \hat{a}_n^\dagger\hat{a}_n^\dagger \times |0_n\rangle = \hat{b}_n^\dagger\hat{b}_n^\dagger|0_n\rangle = 0$. For different sites these operators commute. $\hat{H}_b$ describes a linear aggregate of coupled two-level molecules, the nonlinear optical properties of which have recently been reviewed [4]. $\hat{H}_a$ accounts for

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the third molecular level and $\hat{H}_{ab}$ represents the interaction between two b excitations and one a excitation.

When $|J| \ll \omega_b$, the overall ground state, $|0\rangle$, of $\hat{H}$ is a direct product of the ground states of all molecules. Starting from the ground state, one-photon allowed transitions occur only to the one-exciton eigenstates of $\hat{H}_b$, $|k_b\rangle \equiv N^{-1/2}\sum_n \exp[2\pi i k_b n/N] b_n^\dagger |0\rangle$. These states are the lowest excited eigenstates of $\hat{H}$; they form a band of N states ($k_b = 0, 1, \ldots, N-1$) with transition frequencies $\Omega_{k_b} = \omega_b + 2J\cos(2\pi k_b/N)$. The b one-exciton band governs the linear optics of the assembly. To describe the third-order optical response, we also need the eigenstates that have a dipole-allowed transition from this band. These are found in the next higher band of eigenstates and their space is spanned by two types of states. (i) The N one-exciton states $|k_a\rangle$ of $\hat{H}_a$, which are defined in analogy to the $|k_b\rangle$ and are degenerate with energy $\hbar\omega_a$. (ii) States with two b excitations, for which a convenient basis is $|K, s\rangle = N^{-1/2}\sum_R \exp[2\pi i KR/N] b^\dagger_{R-s/2} b^\dagger_{R+s/2} |0_n\rangle$. Here, $K = 0, 2, \ldots, 2N-2$ and $s = 1, 2, \ldots, (N-1)/2$ for N odd (which we will restrict ourselves to) [8]. The label s cannot be zero, since two b excitations cannot reside on the same site; this Pauli exclusion principle is fully responsible for the nonlinear response in assemblies of two-level molecules. The states $|K, s\rangle$ are not yet eigenstates of $\hat{H}_b$; it is possible to analytically find these eigenstates [8], but here it is more useful to adhere to the present basis. As a result of the translational symmetry the total Hamiltonian mixes only the states $|K, s\rangle$ (all s) with $|k_a = K\rangle$ (k_a even) or $|k_a = K - N\rangle$ (k_a odd). Moreover, $\hat{H}_{ab}$ couples only $|K, s\rangle$ with $s = 1$ directly to the $|k_a\rangle$. Because of this simple coupling, the Green's function $\hat{G}$ within the second band of excited states can be solved analytically through the Dyson equation, $\hat{G} = \hat{G}^0 + \hat{G}^0 \hat{H}_{ab} \hat{G}$, when using the $|K, s\rangle$ representation for the b two excitons. This enables us to calculate any third-order nonlinear optical response function for our system. We finally note that we will restrict ourselves to the optical response of aggregates smaller than an optical wavelength, so that the only dipole-allowed one-photon state is $|k_b = 0\rangle$ and the only dipole-allowed two-photon states have $K = k_a = 0$.

Two-photon absorption from a cw laser beam with linear polarization $\hat{\mathbf{e}}$ and frequency ω, is proportional to $\mathrm{Im}[\gamma(\omega)] \equiv \mathrm{Im}[\hat{\mathbf{e}}\cdot\gamma(-\omega;\omega,\omega,-\omega)\vdots\hat{\mathbf{e}}\hat{\mathbf{e}}\hat{\mathbf{e}}]$, with $\gamma(-\omega;\omega,\omega,-\omega)$ the third-order hyperpolarizability tensor of a single chain [9]. To evaluate $\gamma(\omega)$ we use an equations-of-motion approach similar to that found in Ref. [8] for chains of two-level molecules and use the above described solution for the Green's function in the subspace of two-photon allowed states. We assume the following intramolecular population and coherence relaxation times: $T_{2,b0} = 2T_{1,bb} = 2T_{2,a0} = 4T_{1,aa} = 3T_{2,ab} 1/\Gamma$. Thus, the coherence relaxation rates for the b two excitons and the a one exciton are equal. It is then possible to obtain a simple analytic expression for the TPA spectrum for arbitrary chain size N in terms of a finite summation over the wave number q related to the internal motion [8] of the b two excitons. If N is larger than the coherence size, $(|J|/\Gamma)^{1/2}$, imposed by the damping, [8(b)] the sum can be converted to a contour integral over the unit circle. From this, we find within the rotating wave approximation the closed expression

$$\gamma(\omega) = \frac{4N(\boldsymbol{\mu}_1\cdot\hat{\mathbf{e}})^4}{8\hbar^3} F^2(\omega)F^*(\omega) \times \left\{\frac{1+z}{1-z} - \frac{\beta^2(1+z)^2}{2z^2(1-\beta^2) - \Delta z + 2}\right\}. \quad (2)$$

Here, $F(\omega) \equiv (\omega - \Omega_{k_b=0} + i\Gamma)^{-1}$ is the b one-exciton Green's function, and $\beta \equiv \mu_2/\mu_1 = \tilde{J}/J$. Furthermore, $\Delta \equiv (\omega_a - 2\omega_b)/J$, the deviation of the a state's transition frequency from twice the b state's, and z is given by $z = \alpha \pm \sqrt{\alpha^2 - 1}$, with the laser detuning defined by $\alpha \equiv (\omega - \omega_b + i\Gamma)/2J$ and the important restriction that $|z| < 1$. Equation (2) is our main result, which we analyze in the remainder of this Letter.

The first term in brackets in Eq. (2) agrees exactly with the result obtained for an infinite ring of two-level molecules, which has been analyzed in detail by Spano [8(b)]. Its imaginary part gives rise to a bleaching (negative) and a two-photon absorption (positive) peak for ω near the edge of the b one-exciton band. For $J > 0$, the TPA is redshifted relative to the bleaching feature. From now on, we will mainly focus on the second term in Eq. (2), which incorporates the effect of the third molecular level on the collective TPA. For $J \to 0$, the imaginary part of this term reduces to N times the usual single-molecule two-photon absorption, which has a Lorentzian resonance at $\omega = \omega_a/2$. In general ($J \neq 0$), the second contribution reflects the interference between intramolecular and intermolecular nonlinear optical effects. As will be shown in the following, much of its behavior as a function of the system parameters Δ and β can be extracted analytically.

We first note that the second term gives rise to extra spectral features, as compared to a chain of two-level molecules, whenever its denominator vanishes in the absence of damping. This happens for two values of z, $z_\pm = \{\Delta \pm [\Delta^2 - 16(1-\beta^2)]^{1/2}\}/4(1-\beta^2)$, of which either zero, one, or two lie within the unit circle. Thus, depending on the values of Δ and β, either zero, one, or two additional peaks occur in the TPA spectrum. Straightforward analysis of $z_\pm$ leads to the "phase diagram" in Fig. 1. The two curves that separate the various regions in this diagram are the parabolas $\Delta = \pm 2(\beta^2 - 2)$. In region I, no extra peaks exist, which implies a total absence of intramolecular TPA. In regions II and III, one extra peak exists, which may be compared to the usual intramolecular TPA, except that the peak position and intensity are changed. In regions IV, two extra

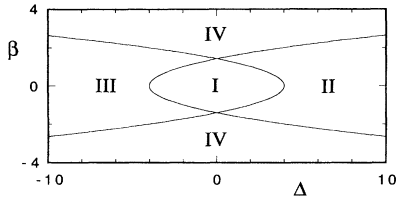

FIG. 1. Phase diagram dividing the parameter plane (Δ, β) in different regions according to the number of extra TPA peaks that may occur due to the third molecular level in a chain of three-level molecules.

peaks occur at each (Δ, β) point: collective effects give rise to a new spectral feature in addition to shifting and renormalizing the molecular TPA. Using the expressions for z and α given below Eq. (2), the peak positions are found to be

$$\omega_{\pm} = \omega_a/2 + z_{\pm}\beta^2 J . \tag{3}$$

The + solution is allowed only for $\Delta < 2(\beta^2 - 2)$ (regions III and IV in Fig. 1) and the − solution for $\Delta > -2(\beta^2 - 2)$ (regions II and IV). It is clearly seen that the interaction J shifts the peak positions away from the single-molecule TPA. Furthermore, it follows from Eq. (3) that the peak positions always lie outside the b one-exciton band (extending from $\omega_b - 2|J|$ to $\omega_b + 2|J|$) and that in region IV the two peaks occur at opposite sides of this band. If (Δ, β) approaches the phase boundary $\Delta = 2(\beta^2 - 2)$ from the left, the position of the + peak approaches the band edge $\omega_b - 2J$; if $\Delta = -2(\beta^2 - 2)$ is approached from the right, the − peak nears the opposite band edge.

The TPA peaks may be investigated further by expanding α in a frequency region of the order Γ around $\omega_{\pm}$. This leads to an expansion for z, which we substitute in Eq. (2) to find Lorentzian line shapes, $I_{\pm}\Gamma^2/[(\omega - \omega_{\pm})^2 + \Gamma^2]$, with intensities

$$I_{\pm} = \pm \frac{4N(\boldsymbol{\mu}_1\cdot\hat{\mathbf{e}})^4\beta^2 z_{\pm}(z_{\pm} + 1)^3}{8\hbar^3 J^2\Gamma(z_{\pm} - 1)^5[\Delta^2 - 16(1 - \beta^2)]^{1/2}} . \tag{4}$$

This result is valid throughout the region of the (Δ, β) plane where the peak under consideration exists, except if the peak position found in Eq. (3) approaches one of the b one-exciton band edges to within a distance of the order Γ. As noted above, this happens if in the phase diagram one of the separating parabolas is approached. In case the boundary $\Delta = -2(\beta^2 - 2)$ is approached from the right, the − peak grows and merges with the predominant nonlinear absorption features at $\omega_b + 2J$ described by the first term in Eq. (2); if the boundary $\Delta = 2(\beta^2 - 2)$ is approached from the left, the + peak nears the opposite one-exciton band edge and its intensity continuously goes to zero. It should be noted that the intensities of both the + and − peaks are in general low compared to the main "two-level" nonlinear absorption feature derived from the first term in Eq. (2); the spectral separation, however, will facilitate their detection in practice. By contrast, *near* the phase boundaries the effects of the extra resonances can be very large. This is clearly demonstrated in Fig. 2, which shows the *entire* nonlinear absorption spectrum as a function of β for $\Delta = 0$. Exactly at the phase boundary ($|\beta| = \sqrt{2}$), the total nonlinear absorption vanishes completely, as can also be seen from Eq. (2) by direct inspection. This can be traced back to the fact that for the parameter values $(\Delta = 0, \beta = \pm\sqrt{2})$ the first and second molecular transitions have energies and dipoles that mimic those of the harmonic oscillator, so that optical nonlinearities can occur only in techniques of order higher than three. This total cancellation of the two-level nonlinear response by a third molecular level occurs only at the "triple points" $(\Delta = 0, \beta = \pm\sqrt{2})$; at other points of the boundary of the phase region I, the two-level nonlinear absorption spectrum is strongly distorted and reduced (on average) by inclusion of the third molecular level.

We now discuss the most important aspects of our results for the different regions of the phase diagram. We first consider the regions II and III, where one additional TPA peak is found. The behavior in these regions is the least surprising, in the sense that the single additional peak may be viewed as N times the single-molecule TPA that has been shifted and renormalized due to the interaction with the b two-exciton states. In particular, in the limit of large detuning of the a level from twice the b level ($\Delta^2 \gg 16|1 - \beta^2|$), the peak position is given by $\omega_a/2 + 2J/\Delta$ and the intensity by $N(\boldsymbol{\mu}_1\cdot\hat{\mathbf{e}})^4\beta^2(\Delta + 2)^3/\hbar^3 J^2\Gamma(\Delta - 2)^5$; if, moreover, $|\Delta| \gg 1$, the TPA peak continuously approaches N times the exact single-molecule result. This is to be expected, since at these large detunings the molecules are effectively uncoupled.

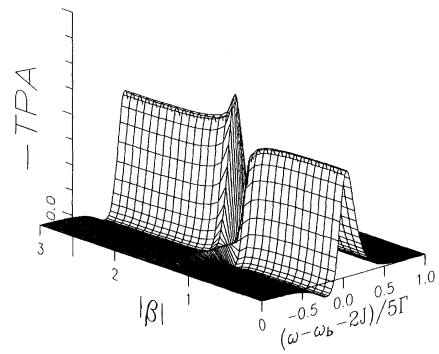

FIG. 2. The total TPA spectrum (in arbitrary units) calculated numerically from Eq. (2) as a function of β for $\Delta = 0$, $J > 0$, and $\Gamma = 10^{-3}J$. For $|\beta| < \sqrt{2}$ (region I), the spectrum remains constant, showing the b one-exciton bleaching and the b two-exciton TPA [8(b)] (notice the minus sign on the vertical axis). Close to $|\beta| = \sqrt{2}$ [to within $O(\Gamma/|J|)^{1/2}$] the third molecular level strongly influences the TPA leading to a dramatic total cancellation at $|\beta| = \sqrt{2}$. As $|\beta|$ increases further the b-exciton line shape is recovered. Note that the dimer peaks for $|\beta| > \sqrt{2}$ are too small to be observed (see Fig. 3).

The most intriguing region of the phase diagram is the one enclosed by the two phase boundary parabolas. In this central region (I), *there is no peak associated with TPA to the third molecular level.* This unexpected behavior arises from the coupling between the a one-exciton state and the b two-exciton states, some of which are strongly two-photon active, but most of which are only weakly or not at all two-photon allowed. As a result, the two-photon oscillator strength related to the a state is greatly diluted and the overall line shape is completely dominated by the b-exciton band [first term in Eq. (2)]. This is clearly observed in Fig. 2. It should be noted that even if the third molecular level does not show up as a separate peak in region I, it may still distort the two-level feature close to the phase boundary. The region over which the distortion is noticeable, however, scales like $\sqrt{\Gamma/|J|}$ and is small for realistic parameter values.

In regions IV, the effect of a third level is manifest in *two* spectral peaks. Here, the increased coupling $|\beta|$ in combination with a sufficiently small detuning (Δ) between the a one-exciton state and the b two-exciton states leads to a new peak. This is somewhat analogous to the occurrence of Fermi resonances in vibrational spectroscopy, where additional Raman active modes arise from accidental resonances between active and inactive modes [10]. If $\beta^2 \gg 1 \gg \Delta^2$, the two peaks in the region IV are positioned symmetrically with respect to the single-molecule TPA position: $\omega_\pm \omega_a/2 \mp |\beta|J$ and have equal intensities, $I_\pm = N(\boldsymbol{\mu}_1 \cdot \hat{\mathbf{e}})^4/2\hbar^3 J^2 \Gamma$. In this limit the Hamiltonian in the two-photon allowed subspace decouples into a chain of length $N - 2$ and a "dimer" subspace, consisting of the states $|k_a = 0\rangle$ and $|K = 0, s = 1\rangle$. The states $2^{-1/2}(|k_a = 0\rangle \mp |K = 0, s = 1\rangle)$ are responsible for the two symmetric features. For decreasing $|\beta|$, the peaks become asymmetric ($I_+ < I_-$) and move toward the b one-exciton band edges. These trends are clearly demonstrated in Fig. 3.

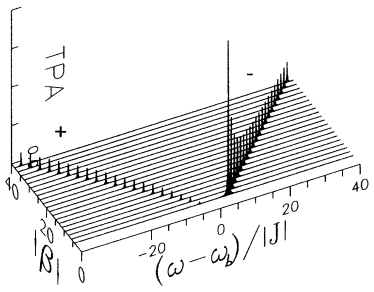

FIG. 3. The two *additional* TPA peaks (in arbitrary units) arising from the third molecular level in the regions IV of the phase diagram calculated numerically from Eq. (2), as a function of $|\beta|$ for $\Delta = 0$ and $\Gamma = 10^{-3}|J|$. To facilitate the presentation, the width of the peaks has been increased by a factor of 100. For $|\beta| \to \sqrt{2}$, the peaks approach the b one-exciton band edges and lose their individual identity (see text). For comparison, the magnitude of the b-exciton bleaching peak (see Fig. 2) is larger than $I_\pm(|\beta| \to \infty)$ by a factor of the order $(|J|/\Gamma)^{5/2}$.

In conclusion, we have shown that for a one-dimensional crystal of interacting three-level molecules, it is possible to calculate the TPA spectrum exactly. We have found that, depending on the system parameters, zero, one, or two additional TPA peaks may arise due to the presence of the third molecular level. Our theory is a step forward towards a more realistic modeling of the nonlinear optical properties of molecular aggregates and clusters, and charge transfer crystals [11], where higher molecular states are usually omitted. In direct analogy to the TPA spectrum, our analysis can be used to determine to what extent the recently observed [5] induced absorption features in pump-probe spectra of J aggregates are caused or influenced by higher molecular levels, or whether these features indeed have a pure multiexciton nature. In this context it is of interest that recent semiempirical calculations indicate that pseudoisocyanine—one of the best-known aggregate forming dyes—has a third (dipole-forbidden) molecular level just above the two-exciton band of the first excited state [12]. The parameters for this particular example place it within region II of the phase diagram and a single intramolecular induced absorption peak should be expected that is well separated from the already observed two-exciton induced absorption. In future work we plan to investigate more detailed relaxation models. It should be emphasized that our methods can be used to calculate all third-order optical response functions for this model system.

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